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The Photochemistry of Poly(methylphenylphosphazene)

by

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The Photochemistry of Poly(methylphenylphosphazene)

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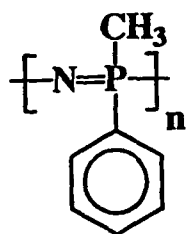
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Introduction

Since 1966, when Allcock¹ first prepared linear, soluble poly(organophosphazenes), interest in polymers with a phosphorus-nitrogen backbone has rapidly increased. One of the most attractive features of poly(phosphazenes) is that, by a proper choice of the substituent group, they become suitable for a variety of technological applications.²⁻⁵ Since poly(phosphazenes), in general, have high resistance to flammability,⁶ there has been considerable interest in commercial application of these materials as fire-resistant coatings and flame-retardant additives.⁷ The thermal stability of several poly(phosphazenes) has been investigated both in solution and in bulk phase⁸⁻¹⁰ owing to their potential use in a variety of situations requiring exposure to higher temperatures. Likewise, since they may well be used for applications requiring exposure to light, a series of investigations on the photochemical behavior of poly(organophosphazenes) has been carried out by Minto *et al*¹¹⁻¹⁸ and Allcock *et al*.¹⁹ To date, photochemical investigations have been performed on poly(phosphazenes) bearing alkoxy/aryloxy or amino substituents on the phosphorus atom. In this report, we will focus our attention on poly(methylphenylphosphazene), PMPP, which has an aromatic phenyl group attached directly to the phosphorus atom of the phosphazene repeat unit. The



PMPP

photophysical behavior of PMPP has been reported in a previous paper.²⁰ In this paper, the photochemical behavior of PMPP is reported with particular emphasis on the role of molecular oxygen in the chain scission.

Experimental Section

All solvents were obtained from Burdick and Jackson and used as received. PMPP was prepared and purified by the method described earlier.²¹ Polymer film and solution irradiations were conducted with either a Rayonet RPR-100 photochemical reactor equipped with a full complement of sixteen 300 nm lamps, a 254 nm Spectroline (model XX-15F) low intensity mercury lamp, or a 450W Canrad-Hanovia medium pressure mercury lamp. All irradiations were carried out at room temperature in the presence of air or nitrogen, as appropriate. A DuPont 9000 thermal analyzer was used for the thermogravimetric analysis (TGA) and DSC scans. DSC and dynamic TGA scans were obtained using 10°C/min temperature ramps. During the TGA experiments a continuous flow of nitrogen gas

was maintained throughout the sample compartment. Polymer molecular weights were determined by size-exclusion chromatography (SEC) on a Waters Associates GPC II instrument with a Waters Maxima data handling system using 500-, 10^4 -, 10^5 and 10^6 -Å μ Styragel columns in series. The SEC operating conditions consisted of a mobile phase of THF containing 0.1% $(n\text{-Bu})_4\text{N}^+\text{Br}^-$, a flow rate of 1.5 mL/min, a temperature of 30°C and a sample size of 0.05 mL of 0.1% solution. The system was calibrated with a series of narrow molecular weight polystyrene standards in the range of 10^3 - 10^6 . The products formed on irradiation were identified by gas chromatography (Hewlett-Packard HP 5890A) using a Hewlett-Packard HP-1 capillary column (crosslinked methyl silicone gum, L = 25 m, ID = 0.32 mm) and a flame ionization detector. Retention times were compared with those of authentic samples.

A Perkin-Elmer 1600 Fourier transform infrared (FT-IR) spectrometer was used for recording infrared spectra. UV spectra were obtained on a Perkin-Elmer Lambda 6 UV-VIS spectrophotometer. Corrected fluorescence spectra were obtained on a Spex Fluorolog-2 spectrofluorometer with 3.5 nm bandpass excitation and emission slits.

Results and Discussion

The UV absorption spectra of poly(methylphenylphosphazene), PMPP, in air-saturated dichloromethane before and after irradiation with 300 nm Rayonet lamps are shown in Figure 1. The absorption band around 240 - 260 nm, due to the perturbed phenyl groups on the phosphazene backbone,²⁰ decreases as the irradiation is performed, whereas the band around 270 nm increases. The decrease in 240 - 260 nm absorption indicates a loss of phenyl groups attached to the -P=N- backbone of the polymer while the new absorption band appearing around 270 nm is due to the photoproducts.

In order to define the impact of irradiation on the thermal properties, PMPP films were photolyzed for periods up to 12 h with the unfiltered output of a medium pressure mercury lamp. Table I shows T_g and TGA onset and mid-point decomposition temperatures before and after irradiation of PMPP film. Although the glass transition does not change appreciably upon irradiation, the TGA onset and mid-point decomposition temperatures decrease dramatically indicating that PMPP undergoes marked photodegradation. The decrease in thermal stability is accompanied by a drop in the molecular weight after irradiation: As seen from the results in Table II, irradiation of PMPP in solution or film in the presence of

oxygen (air) leads to a pronounced decrease in the polymer molecular weight as exemplified by the decrease in the peak maximum molecular weight (based on polystyrene standards). Interestingly, the polymer film, after irradiation in air, remained completely soluble in dichloromethane indicating that a very efficient chain cleavage process with little crosslinking occurs in the photodegradation of the PMPP polymer. In contrast, when irradiation of the film was conducted in a nitrogen saturated atmosphere, extensive crosslinking and gel formation were observed (Table II). The irradiated film was totally insoluble in dichloromethane (the casting solvent) indicating that appreciable crosslinking takes place.

IR spectra of films irradiated in the presence and in absence of molecular oxygen were also recorded. Figure 2 shows the IR spectra before and after irradiation (254 nm Spectrolinc lamp) of a thin film of PMPP in air for 2 h. A significant and uniform decrease in most of the infra-red bands occurs with increasing irradiation time: The bands at $1300\text{--}1296\text{ cm}^{-1}$ and $1195\text{--}1175\text{ cm}^{-1}$, assigned to the P-N-P asymmetric vibration or a degenerate ring stretching mode,²² and the band around 875 cm^{-1} assigned to the P-N-P symmetric stretching, decrease upon irradiation, indicating that degradation of the polymer main chain occurs, in accordance with the molecular weight changes previously noted in Table II. An

increase in intensity is observed between 3400-2600 cm^{-1} , attributed to the formation of hydroperoxide groups on the surface of the polymer film: A similar observation was reported earlier¹⁷ for poly[bis(4-isopropylphenoxy)phosphazene]. A new absorption around 1700 cm^{-1} is attributed to carbonyl groups formed on the film surface, probably derived by thermal and/or photochemical decomposition of hydroperoxides, since the irradiation is conducted in the presence of molecular oxygen.¹⁷ In the presence of nitrogen, no new absorption after irradiation was observed and only a small decrease in the P=N stretchings (bands around 1300, 1187 and 875 cm^{-1}) occurred (Fig. 3). As we will discuss below, when molecular oxygen is excluded, the photodegradation process of PMPP is quite different.

Irradiations were carried out in the presence and absence of oxygen and the formation of small molecule photoproducts was investigated. In each case, biphenyl (determined by gas chromatography) was found to be the major product, with phenol as a minor product. Biphenyl can also be detected by fluorescence spectroscopy: The fluorescence spectra of PMPP in air-saturated dichloromethane recorded upon excitation at 270 nm, both before and after irradiation (300 nm Rayonet lamps), are shown in Figure 4. The disappearance of the red-shifted²⁰ fluorescence around 430 nm and gradual increase in the fluorescence intensity

around 320 nm are indicative of the photodegradation process. The fluorescence spectra of a PMPP film (cast from dichloromethane) in air before and after irradiation are shown in Figure 5. As described in a separate paper,²⁰ the fluorescence maximum of unirradiated PMPP film is blue-shifted compared to the solution spectrum presumably, due to geometry restrictions of the excited state in the film (see reference 20 for a full discussion). As in the case of solution irradiation, the structured emission centered around 320 nm increases as the irradiation is carried out. For both irradiation in solution (Fig. 4) and film (Fig. 5) the 320 nm emission is inferred to be biphenyl by comparison with an authentic sample: The characteristic vibrational fine structure provides strong evidence for biphenyl formation.

The formation of biphenyl upon irradiation of PMPP in solution was monitored by both GC and fluorescence spectroscopy in the presence and absence of 10^{-3} M piperylene, a quencher with a triplet energy (E_T) of 59 kcal/mol. The amount of biphenyl formed was followed by evaluation of the GC peak area. The build-up of the fluorescence intensity at 320 nm was also recorded. No change in the concentration of biphenyl was observed by either method upon irradiation in the absence or in the presence of piperylene (10^{-3} M) indicating that piperylene did

not quench the formation of photoproduct. We have reported²⁰ that 1,3-cyclohexadiene (triplet quencher, $E_T = 54$ kcal/mol) readily quenches the PMPP triplet with a bimolecular quenching rate constant of 5.6×10^9 L mol⁻¹ s⁻¹ determined by laser flash photolysis. The lack of a corresponding quenching of product formation therefore provides evidence that the lowest triplet state of PMPP is not involved in the photochemistry of PMPP, and that the reaction must proceed from an excited singlet state, or a short-lived upper triplet state, or a hot ground state leading to the formation of biphenyl and other products.

In order to explain the photochemical behavior of PMPP in the presence and absence of oxygen, we propose a mechanism (Scheme I) similar to that proposed earlier^{12,13,17-19} for photochemical reactions of other poly(phosphazenes) with alkoxy/aryloxy or amino substituents. We note that biphenyl formation has also been postulated by Allcock¹⁹ for poly(bisphenoxyphosphazene) photolysis. According to Scheme I, the primary act in the photolysis of the polymer is the homolytic scission of the P-C₆H₅ bond in the excited singlet state of PMPP to yield an aryl radical (C₆H₅·) and a macroradical. We postulate that the direct dissociation of a -P=N- skeletal bond *via* a primary photochemical process does not occur in accordance with previous reports.¹⁹ Apparently the -P=N- backbone has an unusual

capacity to dissipate the absorbed energy by processes other than bond cleavage.¹⁹ The phenyl radical, once formed, can abstract a hydrogen atom, e.g., from the solvent, giving benzene, or it can react with oxygen to ultimately yield phenol as shown in Scheme I. We could not identify benzene directly by GC. However, this is not so surprising since it has been reported²³ that benzene itself photooxidizes to unsaturated linear aldehydes: Such species could then undoubtedly degrade by secondary photolysis further to yield carbon dioxide. Formation of biphenyl could occur from two different pathways: (a) phenyl radical phenyl radical combination and/or (b) reaction of the phenyl radical with a substituted phenyl group on the phosphazene chain forming the cyclohexadienyl type radical and thereby giving biphenyl. Indeed, the formation of cyclohexadienyl type radical resulting from the hydrogen abstraction on biphenyl has been previously reported.^{24,25} Although a cyclohexadienyl type radical was not detected directly by laser flash photolysis (see reference 20 for experimental details) in this case, this may well be due to the rapid formation and loss and/or low extinction coefficient of the cyclohexadienyl radical making it impossible to detect within the timescale of our laser flash system (about 15 ns). The polymer macroradical may react by two pathways, depending on the presence or absence of oxygen. If oxygen is present, a peroxidic intermediate on phosphorus can form. The existence of this intermediate is supported by IR studies

that show bands due to O-H stretching. Such band do not appear in the absence of oxygen. It is quite reasonable that the breaking of the peroxidic O-OH bond induces chain scission of the polymer with a decrease in molecular weight in accordance with a similar mechanism reported by Gleria *et al.*^{12,15,17,18} Unfortunately, the formation of P=O groups could not be confirmed by IR spectroscopy since the P=O group absorb in the same spectral region (1200-1300 cm^{-1}) as the asymmetric vibration of the P-N-P group.²⁶ In the absence of oxygen, the formation of inter-chain linkages between two macroradicals is no doubt the dominant process leading to an increase in molecular weight and gel formation.

Conclusions

The photochemistry of poly(methylphenylphosphazene) in dichloromethane solution and film has been investigated. Quenching experiments indicate that the photoreactions most probably occurs from either a first excited singlet state or a short-lived upper triplet state of PMPP. During the irradiation of PMPP, homolytic cleavage of the P-C₆H₅ bond generates biphenyl as the major product with only trace amounts of phenol produced. The macroradical formed as a result of photolysis results in efficient crosslinking gel formation in the absence of oxygen. In contrast, in the presence of molecular oxygen, degradation of PMPP results in

chain-cleavage and a marked reduction in polymer molecular weight. This process results in a severe decrease in the thermal stability of PMPP.

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Table I
Thermogravimetric Analysis and Glass Transitions of PMPP Before and
After 12 h Irradiation.^a

	Before Irradiation (°C)	After Irradiation (°C)
T_g	42	41
TGA (Onset, Mid-point)	424, 463	318, 350

^a450 W medium pressure mercury lamp.

Table II
Peak Maximum Molecular Weight Changes of PMPP Before and After
Irradiation^a

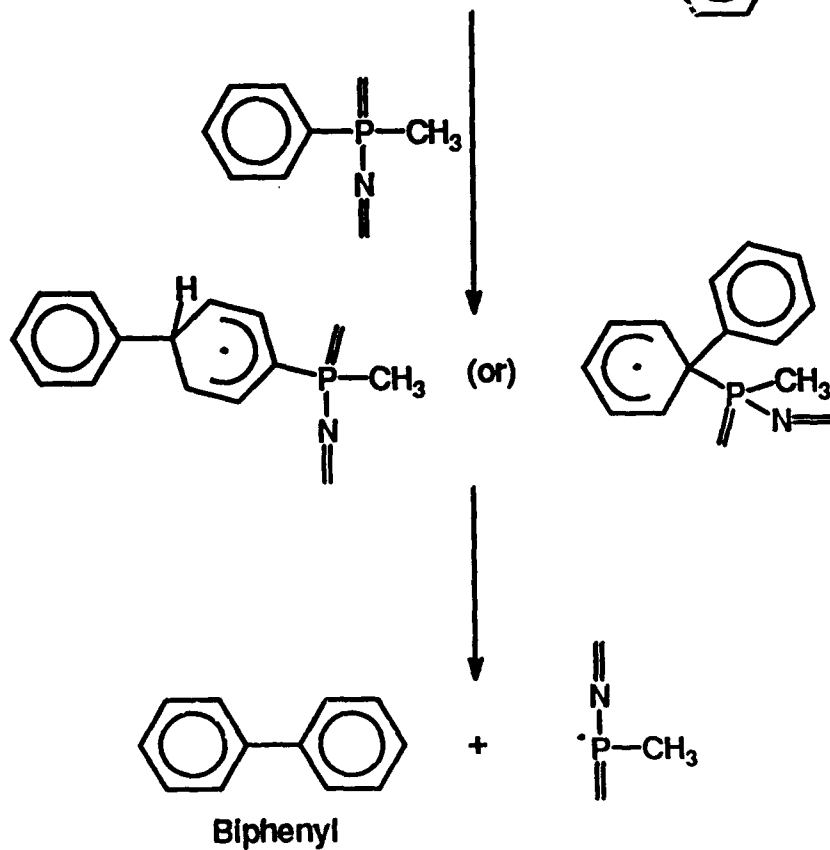
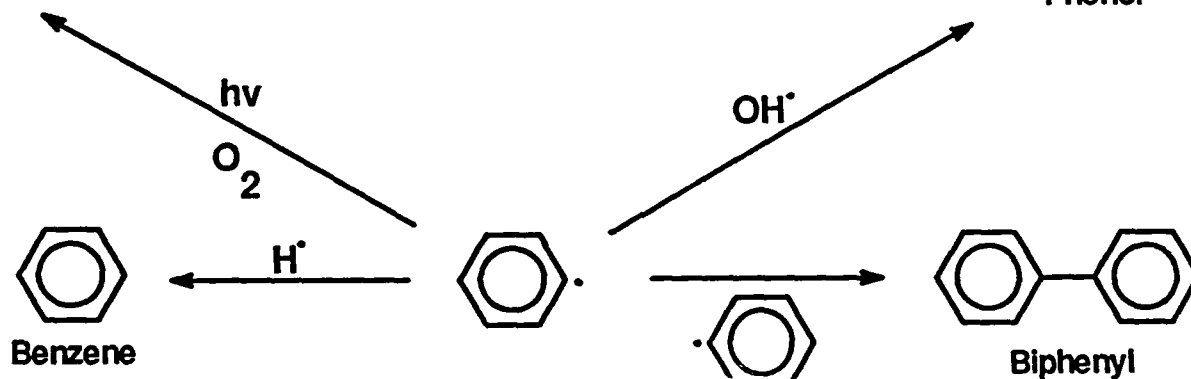
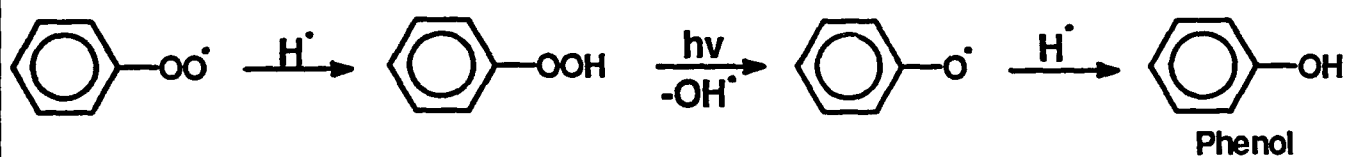
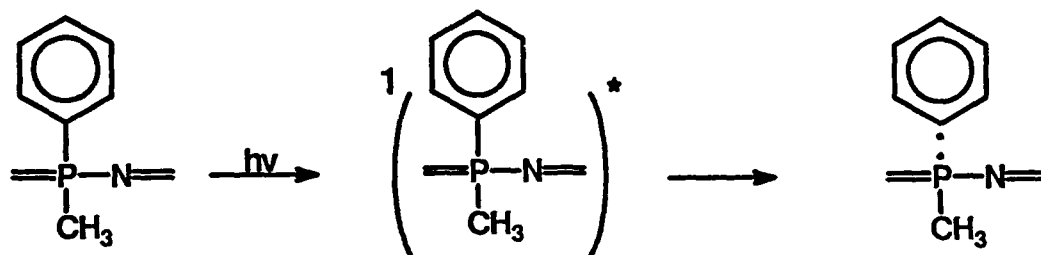
Sample	Medium	Before Irradiation	After Irradiation
THF Solution	Air	73,300	45,300 ^b
Film	Air	73,300	56,300 ^c
Film	N ₂	73,300	gel ^d

^a254 nm Spectroline lamp; ^b3 h irradiation; ^c7 h irradiation; ^dinsoluble

Figure Captions

- Fig. 1. UV spectra of PMPP (0.1 mg/mL) in air-saturated CH_2Cl_2 before and after irradiation using 300 nm Rayonet lamps: (a) 0 min; (b) 30 min; (c) 1 h; (d) 3 h.
- Fig. 2. IR spectra of PMPP film in air, before and after irradiation with a 254 nm mercury lamp: (a) 0 h; (b) 2 h.
- Fig. 3. IR spectra of PMPP film in nitrogen, before and after irradiation with a 254 nm mercury lamp: (a) 0 h; (b) 2 h.
- Fig. 4. Fluorescence spectra of PMPP in air-saturated CH_2Cl_2 (λ_{ex} 270 nm) before and after irradiation using 300 nm Rayonet lamps: (a) 0 min; (b) 30 min; (c) 45 min; (d) 1 h.
- Fig. 5. Fluorescence spectra of PMPP film in air (λ_{ex} 270 nm), before and after irradiation, using 300 nm Rayonet lamps: (a) 0 min; (b) 10 min; (c) 20 min; (d) 30 min.

SCHEME I



SCHEME I (Contd.)

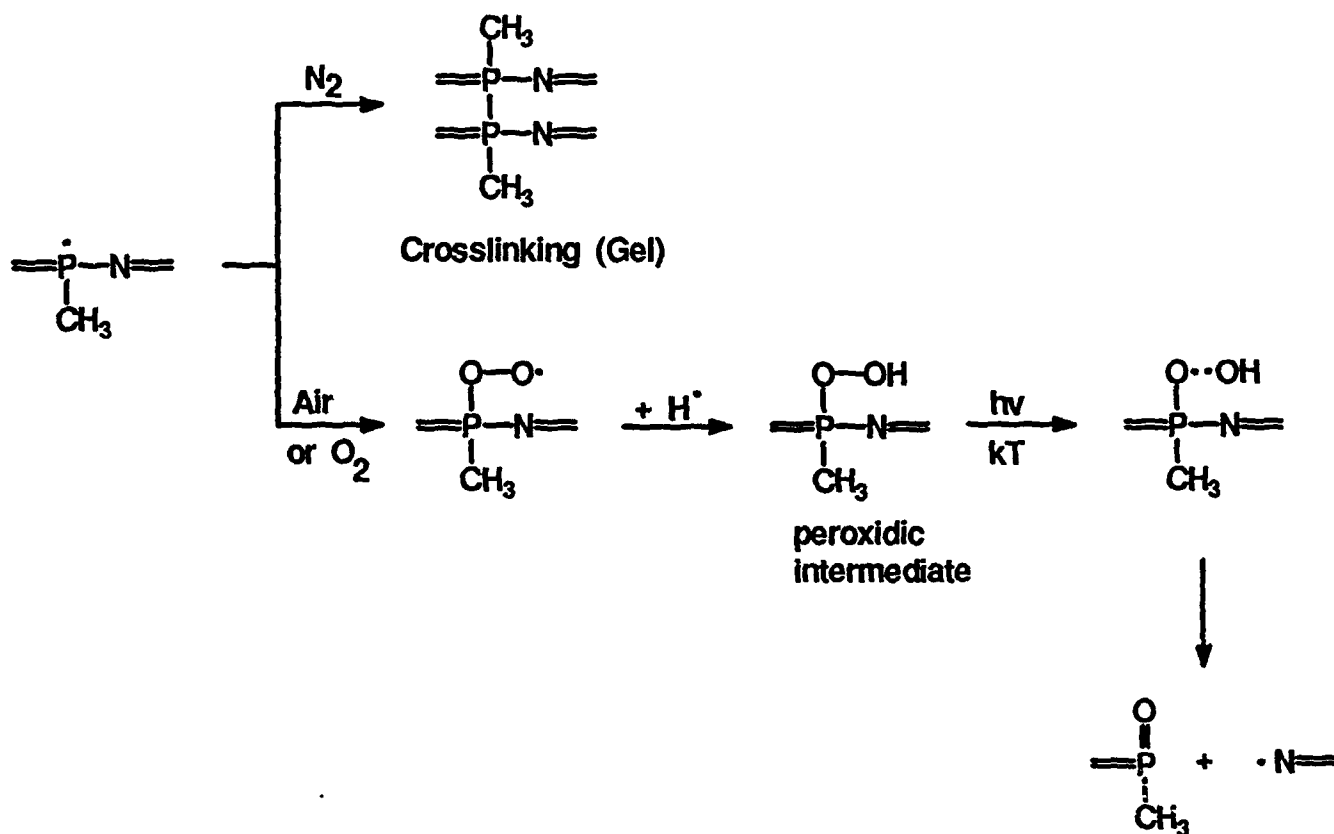


Fig. 1

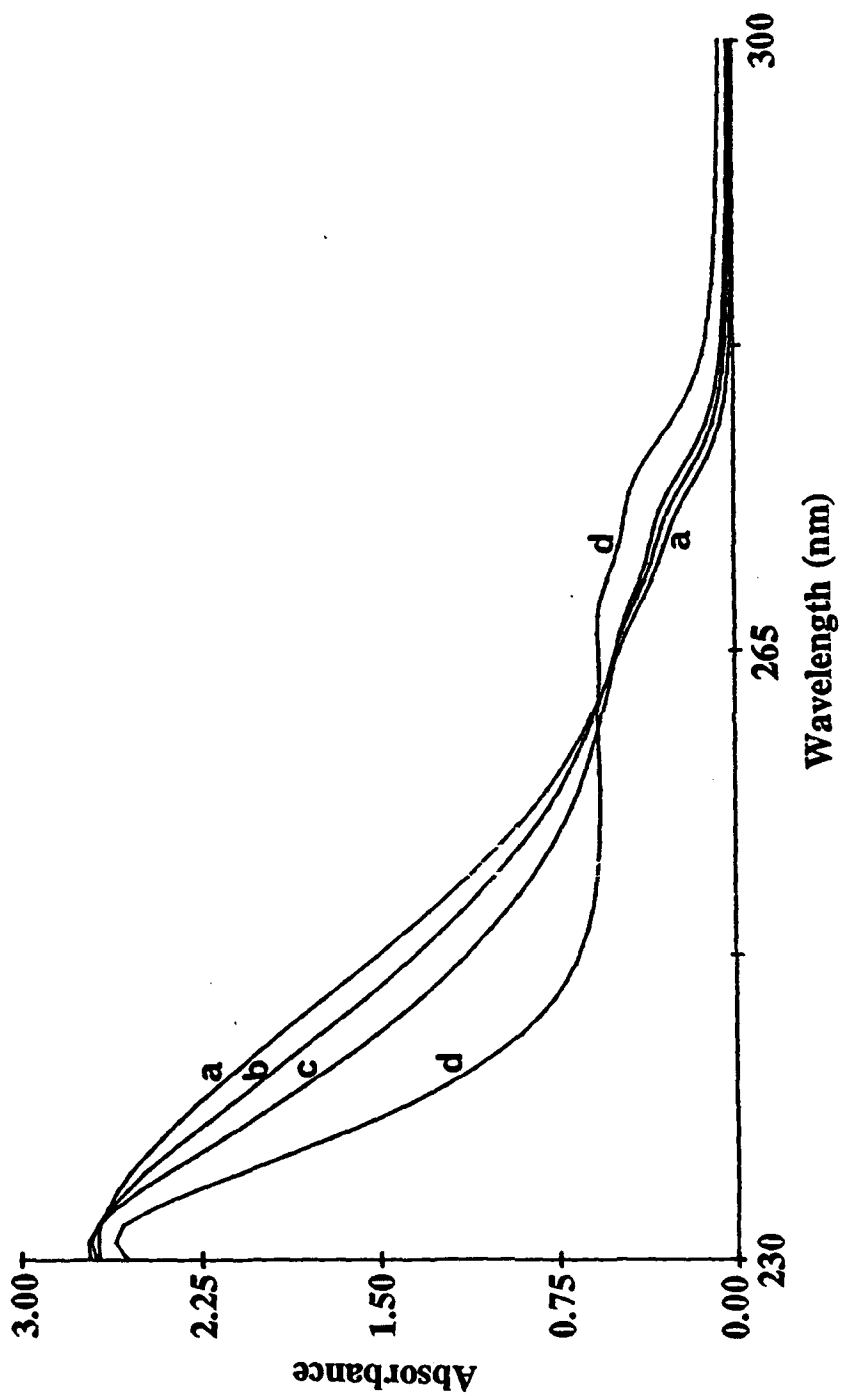


Fig. 2

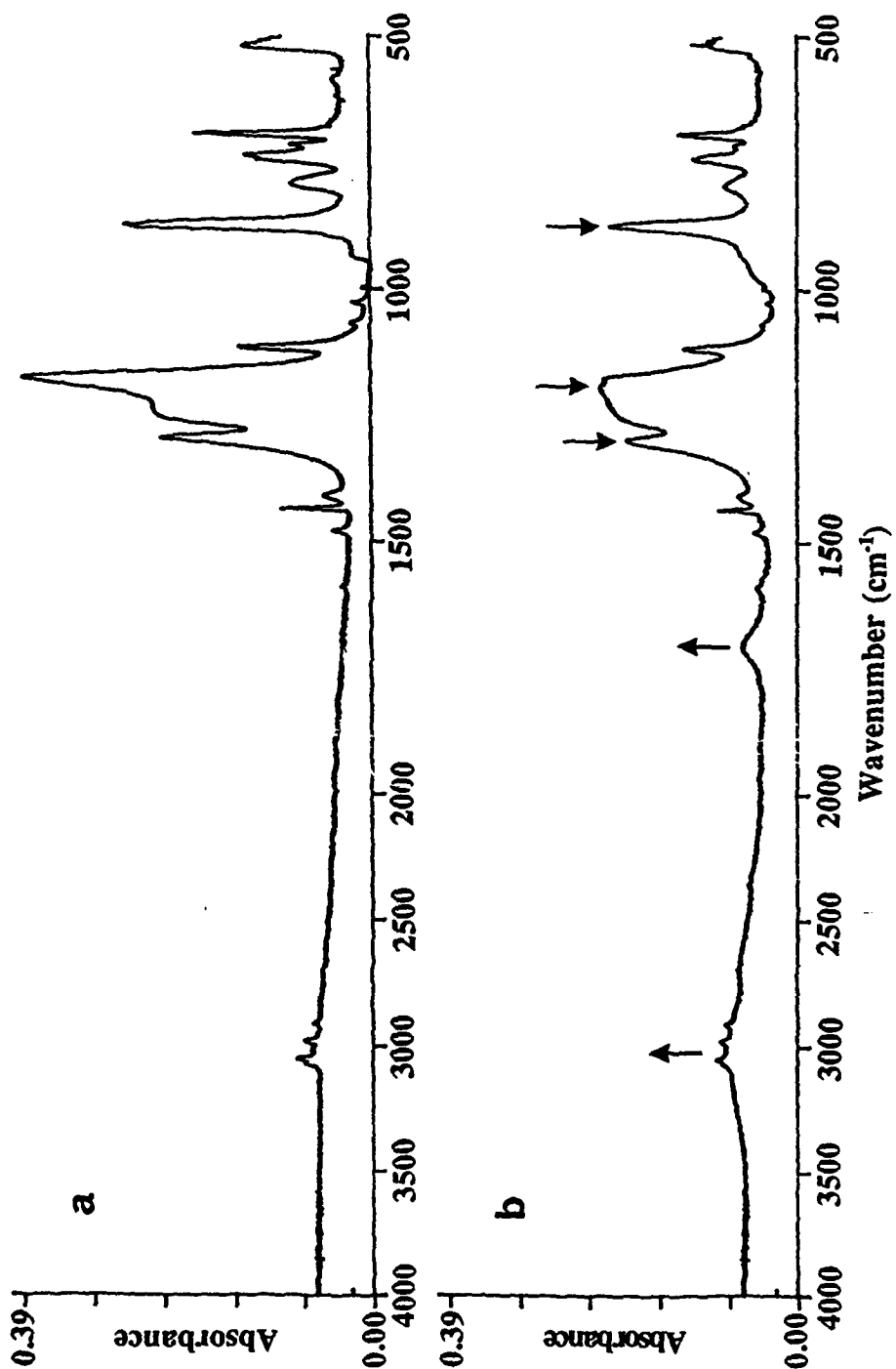


Fig. 3

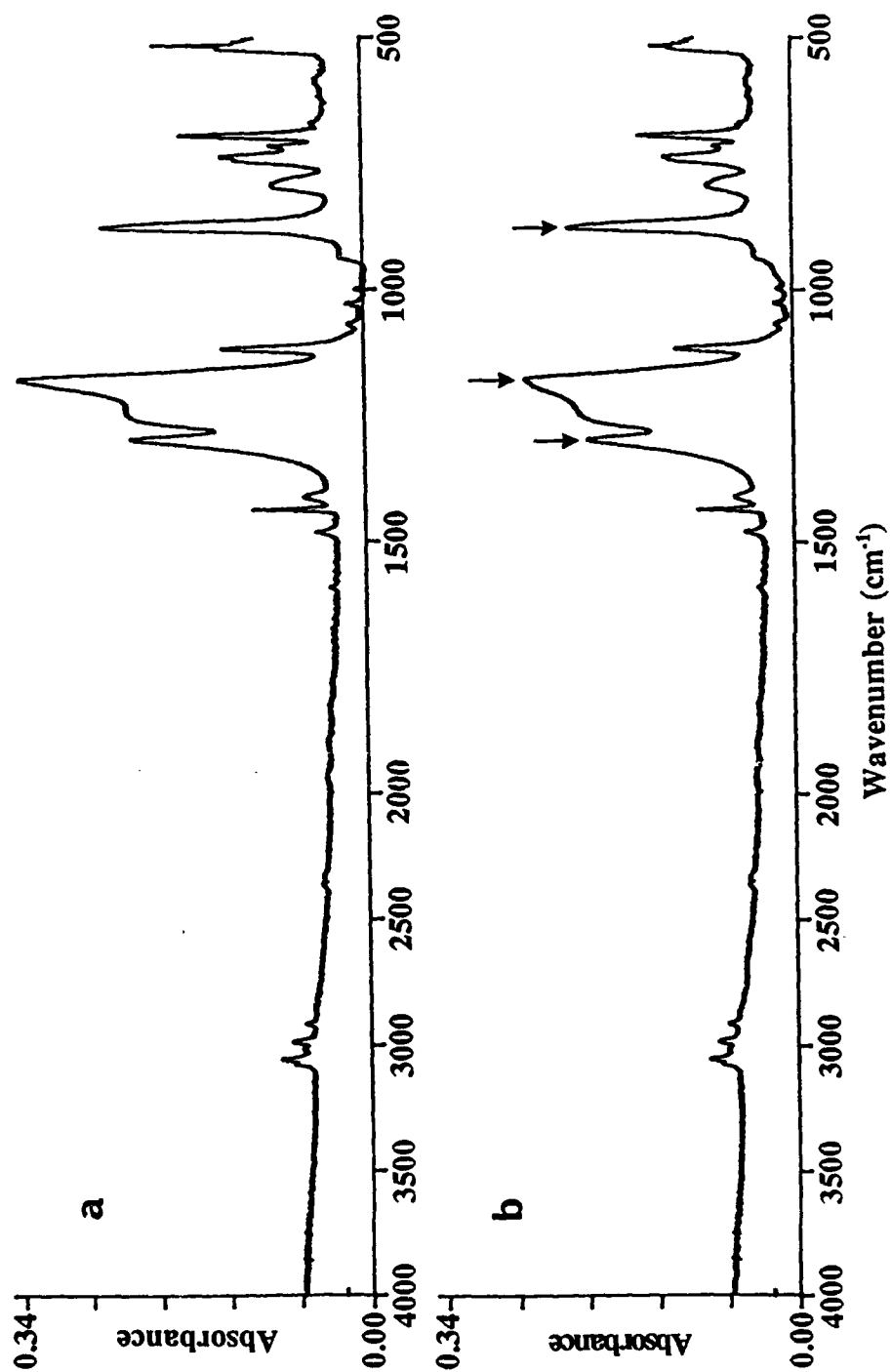


Fig. 4

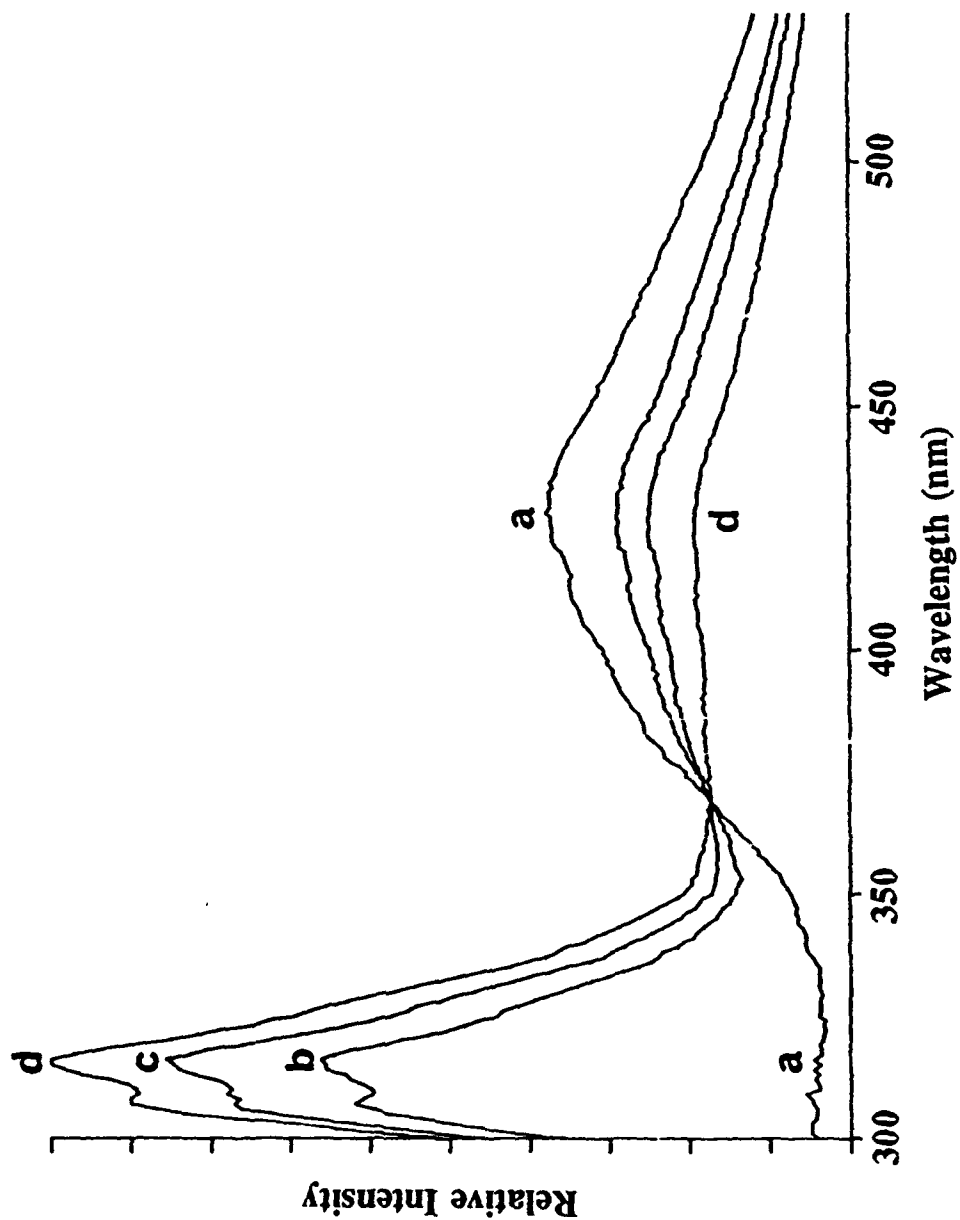


Fig. 5

